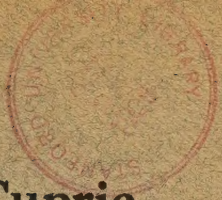
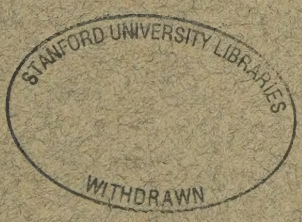


The Free Energy of Cupric Chloride

By RALPH FREDERICK NIELSEN

A THESIS

PRESENTED TO THE FACULTY OF
THE GRADUATE COLLEGE IN THE UNIVERSITY OF
NEBRASKA IN PARTIAL FULFILLMENT OF
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY



3781
N36N

LINCOLN, NEBRASKA
JUNE 4, 1927

UNCLASSED
Dissertation

STANFORD UNIVERSITY LIBRARY

The Free Energy of Cupric Chloride

By RALPH FREDERICK NIELSEN

A THESIS

PRESENTED TO THE FACULTY OF
THE GRADUATE COLLEGE IN THE UNIVERSITY OF
NEBRASKA IN PARTIAL FULFILLMENT OF
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

LINCOLN, NEBRASKA
JUNE 4, 1927

The author wishes to express his sincere thanks to Dr. D. J. Brown, whose suggestions and co-operation have been of the greatest help in carrying out this problem.

THE FREE ENERGY OF CUPRIC CHLORIDE

The Standard Potential of Copper and the Activity Coefficient of Copper Sulfate

This research was undertaken in connection with the attempt to find a standard form of copper for use in potential measurements involving various compounds of copper. The potential of the copper electrode in copper sulfate solution has been measured by numerous investigators, using various forms of copper, and the results always depended on the method of preparing the electrodes. Neumann [1] employed copper reduced with methyl alcohol, electrolytic copper, copper amalgam, and amalgamated copper. Bodländer and Storbeck [2] used copper electrolytically deposited on platinum. We are not quoting their values, since the results are not reproducible and since liquid junctions were employed, rendering it impossible to ascertain the complete cell reactions. Lewis and Lacey [3] give the value of 0.3928 volts for the electromotive force of the cell Cu, $CuSO_4$ (0.05 M), Hg_2SO_4, Hg, using a copper sponge prepared by rapid electrolysis of copper sulfate on a platinum point. They found a considerable number of cells to agree within several tenths of a millivolt, using various current densities in preparing the copper. We have been unable to obtain reproducible results using copper prepared by their method. Sometimes we obtained their values, but invariably the copper lost its reducing activity slowly upon standing under concentrated copper sulfate solution, finally giving values much lower than those obtained by Lewis and Lacey. The following table gives the relative potentials of a sample of copper prepared by this method at the time indicated:

Day	E.M.F.
11/19/26	0.1595
11/23/26	0.1551
11/29/26	0.1531
12/ 3/26	0.1523

In addition, pieces of wire and sheet were heated to a temperature near the melting point of copper in an atmosphere of nitrogen and slowly cooled. These also gave values lower than theirs, although we could not obtain constant results. These facts are in agreement with a rather generally accepted theory that metals freshly precipitated by violent reduction are abnormally high in their reducing power. In fact, a copper sponge obtained by the action of zinc dust on copper sulfate solution gave exceptionally high values.

The reason for the high electromotive forces is of course the fact that the energy stored in the strains must be capable of recovery when the cell operates.

The following relation must hold:

$$-\frac{d(\Delta E)}{dt} = f(\Delta E).$$

where ΔE is the difference between the observed electromotive force and that for unstrained copper. The value of $f(\Delta E)$ must be a positive number for any one value of ΔE and must be larger the larger the value of ΔE. It would be of interest to try to determine this function and to justify it theoretically, and it is the intention of the writer to do so later.

Since we finally decided to use a two-phase electrolytic amalgam in our work, we made a number of measurements involving copper sulfate solution, making use of this amalgam. The amalgam was prepared by electrolysis of a half molal solution of copper sulfate, slightly acidified, using about five amperes per square decimeter of mercury surface, and a copper anode. The amalgam was kept under this solution after preparation. Mercurous sulfate was prepared by electrolysis of a half molal solution of copper sulfate, slightly acidified, using about five amperes per square decimeter of mercury surface, and a copper anode. The amalgam was kept under this solution after preparation. Mercurous sulfate was prepared by electrolysis of a twenty-five per cent solution of sulfuric acid, using about five amperes to a square decimeter and a rapid stirrer which just grazed the mercury surface, according to the method of Hulett.[4] The copper sul-

fate used had been crystallized from an acidified solution of the best C. P. crystals obtainable, and the solutions were made up gravimetrically from a stock solution standardized iodimetrically with metallic copper as primary standard. Conductivity water and distilled mercury were used in preparing the reagents. Measurements were made on a Leeds and Northrup "Type K" potentiometer, using a new Weston cell with a Bureau of Standards Certificate. The thermostat consisted of a bath of distilled water maintained at 25° ±0.05. The mercurous sulfate electrodes were always placed in glass stoppered flasks and rotated in the thermostat for several hours, and then put into dry electrode vessels. An electrode vessel consisted of a test tube into which a side arm had been sealed. A glass tube into which a platinum wire had been sealed was inserted through one hole of a two hole rubber stopper. A stop cock was inserted in the other hole, to allow the solution to flow through the arm of the vessel when necessary. The arm was allowed to dip into one compartment of an H-shaped vessel, the other compartment of which contained the amalgam. The contact with the amalgam was made by platinum, as in the case of the mercurous sulfate electrodes. All heating and regulting circuits were shut off during the measurements, and all connections were made by means of mercury. We measured the following cells, each value being the mean of four different cells, none deviating more than a tenth of a millivolt from the mean. The four cells were obtained by cross combinations among two electrodes of each kind:

Cu(amalgam) $CuSO_4$ (0.05M) Hg_2SO_4 Hg 0.3874 volts
Cu(amalgam) $CuSO_4$ (0.1 M) Hg_2SO_4 Hg 0.3784 volts
Cu(amalgam) $CuSO_4$ (0.2 M) Hg_2SO_4 Hg 0.3697 volts
Cu(amalgam) $CuSO_4$ (0.5 M) Hg_2SO_4 Hg 0.3592 volts

The cell Cu(amalgam) $CuSO_4$(sat) Hg_2SO_4 Hg has been measured by Cohen, Shattaway and Tombrock,[5] by Obata,[6] and by Oholm,[7] using reagents prepared as above. The mean value from the last two investigators is 0.3467 volts ±0.0001. As a check on our preparations we repeated these measurements and obtained 0.3468 volts ±0.0001. Since we were

afraid that we had not washed all the acid from the crystals of copper sulfate before making up our solutions, we recrystallized some from a neutral solution and repeated the measurements at 0.2 M concentration. We obtained perfect agreement with the above, however. Since we found that we could not avoid the formation of a green precipitate at the mercurous sulfate electrode in the case of the 0.05 M solution, this solution contained a drop of nitric acid in a liter of the solution. This should not affect the activity coefficient noticeably if the degree of hydrolysis is small, and indeed was found to have no effect in the 0.1 M solution. We did not think it advisable to carry these measurements into more dilute solutions, owing to the solubility of mercurous sulfate.

As a further check on our activity coefficient we combined our electrodes in the following way:

$Hg\ Hg_2SO_4\ CuSO_4\ (0.1M)\ Cu(amlg)\ CuSO_4\ (0.05M)\ Hg_2SO_4\ Hg$
$Hg\ Hg_2SO_4\ CuSO_4\ (0.5M)\ Cu(amlg)\ CuSO_4\ (0.2\ M)\ Hg_2SO_4\ Hg$
$Hg\ Hg_2SO_4\ CuSO_4\ (0.5M)\ Cu(amlg)\ CuSO_4\ (0.1\ M)\ Hg_2SO_4\ Hg$

These cells gave respectively.

0.0089 volts ±0.0001
0.0105 volts ±0.0001
0.0190 volts ±0.0001

This combination was accomplished by allowing the arms of the two mercurous sulfate electrodes to each dip into one arm of a U-tube, the bottom part of which contained the amalgam, and the top part of which contained the two given solutions.

Since we could not use mercurous sulfate in the dilute solutions owing to its solubility, we tried to measure the cell Cu(amalgam), $CuSO_4$(0.01 M), $CuSO_4$(0.002 M), Cu(amalgam) which gave–0.0210 volts. The liquid junction was established by the method used in the first series of measurements, and was easily reproducible to a tenth of a millivolt. It was found impossible to set up the cell without obtaining cuprous oxide at the electrodes, probably due to the joint action of air and the other substances present. However, in some of our other measurements this was found to have no noticeable effect. In order to avoid this we added to each solution about one twentieth of its molality of nitric acid in

a very small quantity of water. This changed the reading to −0.0164 volts. For the same cell using 0.05 M against 0.1 M solution we obtained 0.0064 volts, and using 0.1 M against 0.2 M solution 0.0062 volts. These values were all easily reproducible to a tenth of a millivolt.

The readings in the second table should be the difference between corresponding readings in the first table. The reason for this is of course the fact that only copper ions can be transported across the amalgam, so that the total cell reaction is simply

$$CuSO_4(c_1) = CuSO_4(c_2).$$

In case we had used copper electrodes in solutions c_1 and c_2 with an amalgam junction, the electromotive force would be zero, since nothing would be added to or subtracted from either solution. This has also been confirmed experimentally. It follows therefore that if we use concentration cells with liquid junctions the electromotive force is proportional to the transport number of the ion of opposite sign to that which is entering at the electrodes. These considerations show the absurdity of speaking of "liquid potentials" rather than merely considering the total cell reaction, since the electromotive force can be a measure of only two factors: the free energy of the chemical changes, and the free energy of the dilutions.

In spite of the fact that the measurements involving liquid junctions were reproducible, division by the transport numbers give high values for the free energy of dilution of copper sulfate. Several causes may be given for this. First, the fact that the transference number is not constant over the range of concentrations may cause a summation of free energies of dilution in the gradient portion sufficient to be measured. Second, if the salt is relatively more hydrolized in the dilute solution, then whenever hydrogen-ion is transported H_2SO_4 is replaced by $CuSO_4$ in the more dilute solution, while $CuSO_4$ is replaced by H_2SO_4 in the more concentrated solution. Since the concentration of H_2SO_4 is relatively less in the more concentrated solution, owing to a lower degree of hydrolysis of the salt, this change occurs with a decrease

in free energy, and an abnormally high electromotive force results. In the case of the cell which dropped from 0.0210 to 0.0164 volts upon addition of acid, the results can hardly be explained, since complications had arisen from the formation of cuprous oxide and the addition of a relatively large amount of acid. We shall not use the cells with liquid junctions in our calculations, but believe that the above considerations suggest an interesting field for investigation.

Employing the values of the two tables, we obtain the following series of activity coefficients:

M	γ
0.05	0.216
0.1	0.153
0.2	0.107
0.5	0.0644
1.38	0.0378

The value of γ for the 0.05 M solution was taken from Lewis and Randall.[15] These values are about three per cent lower than theirs, but are undoubtedly more nearly correct, since their calculations from freezing point measurements were not corrected for the heat of dilution.

For the standard potential of copper amalgam we obtain –0.3502 volts, based on the mean activity of the ions in copper sulfate solution. The copper amalgam used above seems to be a good standard form of copper for use in potential measurements. It is easily reproducible and, being a two-phase amalgam, its potential is independent of the relative quantities of copper and mercury, within rather wide limits. The General Electric Company has prepared single unstrained crystals of copper, and we attempted to obtain some from them, to see if they would give the same potential as the amalgam. They had none on hand, however, which had not been strained, so we did not perform this experiment.

The Copper Amalgam-Cuprous Chloride Electrode

The copper-cuprous chloride electrode has been measured by Immerwahr,[8] by Luther and Wilson,[9] and by Noyes and Chow.[10] These investigations are subject to the errors of not using a reproducible form of copper, of not preparing the electrodes in the absence of oxygen, and of not rotating the

electrodes to insure equilibrium. Luther and Wilson employed the cell Cu CuCl KCl(N/20) N.E. Noyes and Chow employed the cell Cu CuCl HCl H_2. Immerwahr used the cell Cu CuCl KNO_3(N) and HCl(N/20), N.E., in which the complete cell reaction is obviously doubtful.

In our work we first used the cell Cu(amalgam) CuCl HCl HgCl Hg, since it has the advantage of having an electromotive force practically independent of concentration. We tried to follow the method of Ellis [11] in preparing the calomel electrodes, since he obtained results which varied only a few hundredths of a millivolt. We were, however, unable to obtain constant values, and when we rotated the calomel electrodes for a day or two, as he recommends, we obtained values which were nearly ten millivolts too high, as indicated by comparison with hydrogen electrodes. For this reason we employed the cell Cu(amalgam) CuCl HCl H_2.

The copper amalgam was the same as that used above. Cuprous chloride was prepared directly in the electrode vessel by addition of a solution of chloro-cuprous acid to water, while a stream of purified nitrogen bubbled thru the vessel. The chloro-cuprous acid was prepared by reduction of a hydrochloric acid solution of cupric chloride with copper. The amalgam, the supply of which was always kept under an acidified copper sulfate solution, had been previously put in the vessel after washing. The glass stopper was then inserted, and the solution brought to the proper concentration by repeatedly forcing out the solution with nitrogen and drawing in a solution of the required concentration. After drawing in each fresh supply, nitrogen was bubbled thru the cell for a short time and the cell was shaken a few times. The solutions were often kept at about 40° to insure larger crystals and more rapid settling of the salt, and this seemed to have no influence on the results. The last addition of the solution was always below 25° so as to avoid any inrush of solution into the vessel when the stopcocks were opened for the potential measurements. The diagram shows the electrode vessel connected up for filling. The electrode was rotated in the thermostat four or five hours before measuring. Longer periods did not change the potential.

The hydrogen electrode consisted of a piece of platinized platinum foil. The electrode was prepared from clean platinum foil by electrolysis of a solution of chloro-platinic acid containing one per cent platinum. A four volt battery was used, and the current reversed every few minutes for one hour, as recommended by Ellis. The hydrogen entered the vessel at the bottom and escaped thru a trap. The platinum foil was only partially submerged in the solution. Hydrogen was prepared by electrolysis of sodium hydroxide solution, and was passed thru sulfuric acid before entering the preliminary washer, which was kept in the thermostat and contained the same solution as the electrode vessel. Rubber connections were kept at a minimum, and whenever they were used they were paraffined. In one of our measurements two hydrogen electrodes were used, the one receiving electrolytic hydrogen and the other hydrogen prepared from zinc and hydrochloric acid. The hydrogen from the latter source was passed thru concentrated KOH and over P_2O_5 before entering the preliminary vessel. The difference in potential between the two electrodes was less than a hundredth of a millivolt. The hydrogen and cuprous chloride electrodes were joined thru a beaker of the given solution, the arm of the cuprous chloride vessel having been protected by a plug during rotation in the thermostat. Both electrodes were set up four or five hours before being measured.

The hydrochloric acid solutions were made up from conductivity water and weighed quantities were standardized with barium hydroxide, which in turn had been standardized with benzoic acid. Checks were obtained in all the titrations except as noted below. All other manipulations were the same as for the copper sulfate cells.

In the following table the first column gives the molality of the acid, the second column the partial pressure of hydrogen after correcting the barometer reading for temperature and subtracting the vapor pressure of the solutions, assumed equal to that of water. The third column gives the observed electromotive force, the fourth column the activity coefficient interpolated from the table of Lewis and Randall,[12] and the last column the calculated standard potential of the electrode:

M	p	E		E_0
0.0263(?)	705	—0.32638	0.882	—0.13076
0.0263	700	—0.32592		—0.13053
0.02029	700	—0.33615	0.893	—0.13116
0.02029	689	—0.33592		—0.13113
0.00757	695	—0.38250	0.933	—0.12915
0.00757	698	—0.38248		—0.12907
0.03234	697	+0.30830	0.874	+0.13116
0.03234	692	—0.30805	0	—0.13100

The close agreement of each pair shows that the discrepancies are not from faults in the experimental work. Since the solubility of cuprous chloride must play a part in algebraically raising the calculated values of E_0 in the more dilute solution, we shall omit these values. In the case of the first two values we had not obtained checks on the standardization of the solution before it was thrown out, and we therefore believe that we are safe in saying

Cu(amalgam), CuCl(s), Cl^-; $E_0 = -0.1311 \pm 0.0002$.

We recommend this electrode highly as a standard in solutions of chloride-ion between 0.02 and 0.1 molal. In very dilute or very concentrated solutions the solubility of cuprous chloride becomes noticeable.

Study of the Cell CuCl (s) $CuCl_2$ (aq) Cl_2 (g)

This is of course the only combination of electrodes which we could use if we wish to avoid liquid junctions, since copper and mercury would cause precipitation of cuprous chloride from the cupric chloride solution. The CuCl-$CuCl_2$ electrode was studied by Luther and Wilson [13] who measured the cell CuCl, $CuSO_4$ and KCl (each MV/20), N.E. Obviously we cannot use this measurement in our calculations.

With the exception of the preparation of the chlorine electrodes, all procedure was the same as given above. The diagram shows the chlorine electrode in the process of being partially filled with a solution of chlorine in carbon tetrachloride. The vessel was about half filled with this solution, then about two thirds of the remaining space filled with the cupric chloride solution. This method of filling was preferred to filling by suction, since by this method we could avoid loss

of chlorine. The solution in the reservoir contained such a concentration of chlorine as would give a partial pressure of less than a twentieth of an atmosphere, these low pressures being necessary according to the work of Lewis and Rupert [14] on the chlorine electrode. The stop cock C was opened occasionally for an instant to relieve the partial vacuum caused by depletion of the solution. The chlorine used was taken from a cylinder, being passed through water and fused calcium chloride before being passed into the carbon tetrachloride. A small quantity of C. P. carbon tetrachloride was saturated at atmospheric pressure, and then diluted with the required amount of pure carbon tetrachloride. In order to standardize the solution, the electrode vessel was filled in the way described, except that 0.04783 molal HCl was used instead of the cupric chloride solutions, and the electrode measured against a hydrogen electrode in the same solution. With the partial pressure of hydrogen at about 700 mm. this cell gave 1.473 volts in the case of the solution used for the 0.02 M electrodes and 1. 471 volts in the case of the solution used in the other electrodes. Using activity coefficients as above, we find that 0.049 and 0.051 volts respectively must be added to all our measurements to obtain the value that would be given by chlorine at unit activity or fugacity. The electrode was rotated in the thermostat for about an hour. Repetitions for both electrodes gave checks within a millivolt.

The cupric chloride solutions were made up gravimetrically with conductivity water from a stock solution which had been standardized iodimetrically. The stock solution had been made up from crystals of the dihydrate, obtained by recrystallization of the best C. P. product, from a solution containing excss of HCl. These crystals were dried in a vacuum dessicator containing soda lime. The solutions were kept in pyrex flasks, over which a watch glass had been sealed with paraffin. The saturated electrode was set up by adding excess of the dihydrated salt to the electrode vessel.

In the following table, the first column gives the molalities, the second the observed electromotive forces, and the third the activity coefficients, that for the 0.02 molal solution being taken from the tables of Lewis and Randall for similar salts:

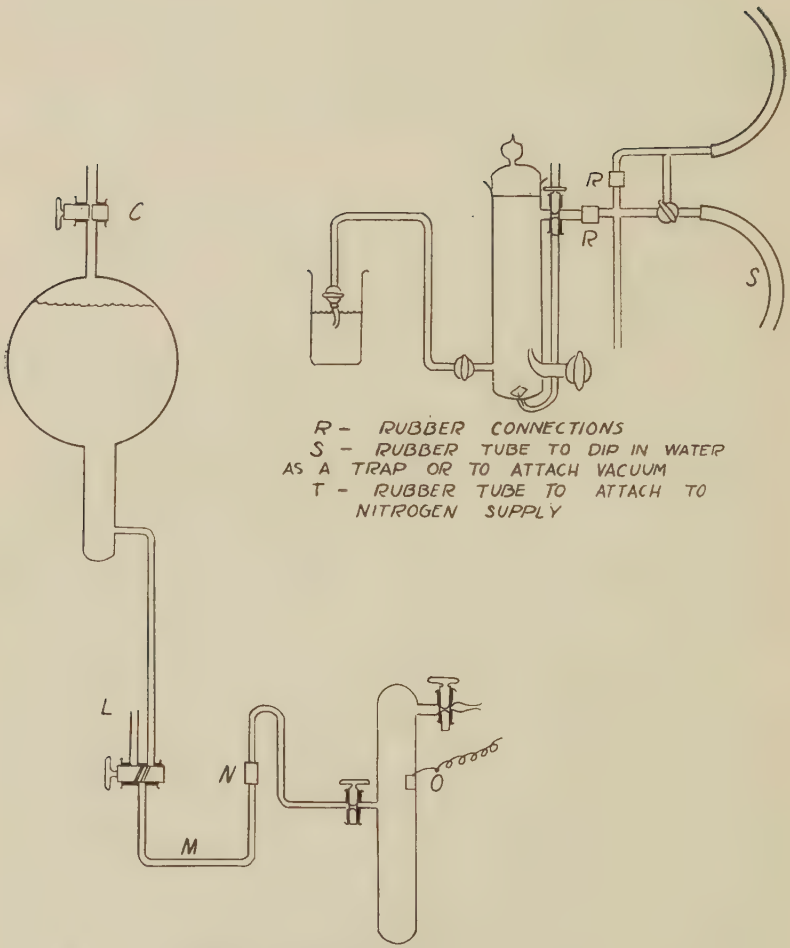
M	E	γ
0.02	1.038	(0.60)
0.05	0.991	0.5
5.82[16]	0.614	0.5

The more dilute solutions contained about a drop of nitric acid in 500 cc. of solution, to prevent the formation of a green precipitate, as in the mercurous sulfate electrodes.

Finally, combining our data and taking 0.65 from Ewan and Ormandy [17] for the activity of the water in the saturated solution, we obtain

$$Cu\,(\text{in sat. amalgam}) + Cl_2\,(g) + 2H_2O\,(l) = CuCl_2 2H_2O;$$
$$\Delta F^\circ_{298} = -44{,}200 \text{ cal.}$$

Various causes may be given for the trend of the activity coefficient in the very concentrated solutions. Debye and Hückel [18] account for the activity coefficients in dilute solutions on the assumption that the deviation from the Nerst equation is due to the work of separating the ions on dilution, on account of their charges, assuming Boltzmann's distribution law and complete dissociation. Hückel [19] has extended the theory, correcting for the change of dielectric constant with concentration, and accounts for the fact that the activity coefficient often passes through a minimum as the solution becomes concentrated. Scatchard [20] has suggested that hydration may be another factor in determining the trend of the activity coefficient. In the case of the hydrogen halides, the rise of the value of γ in concentrated solutions may be largely attributed to a greater tendency to form the molecular species than given by Ostwald's dilution law, since $a_\pm = k\sqrt{p}$, where p is the vapor pressure of the halide. Undoubtedly many factors enter into consideration for the concentrated cupric chloride solutions, including hydration, formation of complex chloride ions, etc. The factors are undoubtedly linked up with the color changes, the color changing from dark green to a dark reddish brown on saturation with cuprous chloride. The problem of the last electromotive force measurement is further complicated by the fact that an enormous quantity of cuprous chloride is dissolved, this probably not only changing the activity coefficient but causing a rather pronounced liquid junction.



R - RUBBER CONNECTIONS
S - RUBBER TUBE TO DIP IN WATER AS A TRAP OR TO ATTACH VACUUM
T - RUBBER TUBE TO ATTACH TO NITROGEN SUPPLY

L - TO CLEAN OUT TUBE M WITH AIR
N - RUBBER CONNECTION
O - PLATINUM IRIDIUM FOIL

BIBLIOGRAPHY

[1] Z. physik. Chem., *14*, 193 (1894).

[2] Z. anorg. Chem., *31*, 458 (1902).

[3] J. Am. Chem. Soc., *36*, 804 (1914).

[4] Phys. Rev., *32*, 321 (1900).

[5] Z. physik. Chem., *60*, 706 (1907).

[6] Proc. Phys.-Math. Soc. Japan, (3), *2*, 223 (1923).

[7] Meddelanden fran Vetenskapsakadiems Nobelinstitut, *5*, N:04 (1923).

[8] Z. electrochem., *7*, 477 (1900).

[9] Z. physik. Chem., *34*, 488 (1900).

[10] J. Am. Chem. Soc., *40*, 739 (1918).

[11] J. Am. Chem. Soc., *38*, 737 (1916).

[12] Lewis and Randall, Thermodynamics, McGraw-Hill Book Co. (1923).

[13] See Note 9.

[14] J. Am. Chem. Soc., *33*, 299 (1911).

[15] See Note 12.

[16] Reicher and Deventer, Z. physik. Chem., *5*, 559 (1890).

[17] J. Chem. Soc., *61*, 775 (1892).

[18] Physik. Z., *24*, 185 (1923). See also Noyes, J. Am. Chem. Soc., *45*, 1080 (1924).

[19] Physik. Z., *26*, 93 (1925).

[20] J. Am. Chem. Soc., *47*, 2096 (1925).